JOURNAL
OF THE
WASHINGTON ACADEMY OF SCIENCES

VOL. 22 MARCH 4, 1932 No. 5

CHEMISTRY.—*Hydration of the solute ions of the lighter elements.*[1]

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INTRODUCTION

The researches carried out by Jones and his collaborators in the Chemical Laboratory of the Johns Hopkins University over a period of years and reported in various papers,[2] developed several independent lines of evidence, each of which pointed to the existence of hydrates in aqueous solutions. These researches may be said to constitute one of the fundamental bases of a relationship which in subsequent years has become widely recognized as an intimate one. At the present time the validity of a relationship between solute ions and their solvent is scarcely to be questioned.

The relationship between solute ions and solvent appears to be one of attraction, somewhat comparable with that characterizing many electrolytes crystallizing out of saturated solutions under certain conditions to form hydrated crystals. In the latter instance, however, a definite and usually integral number of water molecules is recognized as incorporated with each salt molecule. The relationship in both cases is termed hydration, but our knowledge of the specific molecular values involved in solutions is not sufficient to permit any precise evaluation corresponding with the use of the term as applied to crystals.

As a matter of fact we can find little satisfaction in our knowledge of the hydration of solute ions. We may observe that the velocity of a solute ion is not what we had expected it would be,—and may say that the ion is hydrated. We may note that a solute ion does not

[1] Received December 18, 1931.

[2] Amer. Chem. Journ. **23**: 89, 1900; **31**: 303, 1904; **33**: 584, 1905; **37**: 126, 1907. Carn. Inst. Wash. Pub. **60**: 80, 1907; **180**: 1913, and others.

depress the solubility of gases to the extent anticipated,—and may say that the ion is hydrated. We may find other real or apparent inconsistencies,—and attribute the results to the hydration of the ions. In resorting to the generalization we may often be correct,—but our explanation can scarcely become productive until our information is sufficient to permit mathematical expression.

Following a study of the hydration of ions over a period of several years, the writer has become convinced that a better understanding of this subject holds much of promise for the establishment of a more satisfactory interpretation of various inter-related solution phenomena. In outlining some of the reasons for such a conviction as a possible contribution to the subject it will be necessary to make two simple assumptions at the outset. These are (1) an inverse integral relationship between the anhydrous weight of a solute ion and the degree of its hydration, and (2) an orderly change in weight accompanying ionization. There are obvious objections to both these assumptions, and the objections may be sustained throughout the inquiry. Nevertheless, some of the suggested relationships which appear to follow the assumptions are of more than passing interest. A number of such relationships touching upon the characteristics of the solute ions of the lighter elements will be considered in this paper.

Electrical Conductivity as an Index of Velocity and Hydration

Following the first assumption we may examine the observed electrical conductivities of simple solute element ions of the lighter elements and obtain the order of hydration indicated by the relative velocities of the ions. With univalent ions such as Na^+ and K^+ the conductivities and velocities may be considered to be of the same order, and through the extension of Graham's Law the relative velocity values of the ions Na^+ and K^+ (as derived from observed measurements of conductivity through the use of transference data) become indices of relative hydration. The assumption of hydration on an inverse integral basis requires that a succession of weight values be characterized by regular intervals. Such a requisite regularity does not characterize the observed combining weights of the lighter elements, but is found in their atomic numbers. These numbers may be brought to the O = 16 scale by doubling, in which case a tentative series of regular weight values is attained as a basis upon which to project an assumed inverse integral hydration. The following con-

ductance values for the ions Na^+ and K^+ at 18°C. are given by Nernst:[3] $K^+ = 65.3$, $Na^+ = 44.4$. These values, considered as relative velocities, permit the assumption of an inverse integral hydration only when the weight 38, representing potassium, has four water molecules attached, and the weight 22, representing sodium, has twelve water molecules attached. The weight, hydration and velocity values which

TABLE 1.—WEIGHT, HYDRATION AND VELOCITY VALUES CALCULATED FOR THE LIGHTER ELEMENTS THROUGH AN EXTENSION OF GAS LAWS IN RELATION TO OBSERVED ELECTRICAL CONDUCTIVITIES

A.N.	E	Assumed as W. $2 \times$ A.N.	V_1	Postulated Number of Water Molecules	Mol. Wt. Water of Hydration	Mol. Wt. Hydrated Molecule	V_2
0	—	0	—	23	414	414	491
1	H	2	7082	22	396	398	501
2	He	4	5000	21	378	382	512
3	Li	6	4090	20	360	366	523
4	Be	8	3546	19	342	350	535
5	B	10	3162	18	324	334	547
6	C	12	2887	17	306	318	561
7	N	14	2672	16	288	302	575
8	O	16	2500	15	270	286	591
9	F	18	2357	14	252	270	609
10	Ne	20	2236	13	234	254	627
11	Na	22	2132	12	216	238	648
12	Mg	24	2041	11	198	222	671
13	Al	26	1961	10	180	206	698
14	Si	28	1890	9	162	190	726
15	P	30	1826	8	144	174	758
16	S	32	1768	7	126	158	796
17	Cl	34	1715	6	108	142	839
18	A	36	1667	5	90	126	891
19	K	38	1622	4	72	110	953
20	Ca	40	1581	3	54	94	1031
21	Sc	42	1543	2	36	78	1133
22	Ti	44	1508	1	18	62	1271
23	V	46	1474	0	0	46	1474

thus develop for the lighter elements from the assumed inverse integral relationship in conjunction with observed electrical conductivities are brought together in Table 1.

In Table 1 the first column gives the atomic number of the element, the second column gives the chemical symbol of the element, and the third column gives the atomic number transposed to the familiar O = 16

[3] Citation on page 177 in Bayliss, W. M. *Principles of General Physiology*. 1915.

scale as an expression of weight. The fourth column gives the reciprocals of the square-roots of these weight values, multiplied by 10^4 for convenience in manipulation. These reciprocal values represent theoretical relative velocities as derived through the extension of Graham's Law under an assumption of *no hydration*, and on this account they have been designated as V_1 values. The fifth column gives the numbers of water molecules which must be postulated as characterizing hydration when an inverse integral relationship between weight and hydration is associated with the observed relative conductances of potassium and sodium considered as of weight 38 and 22 respectively. The sixth column gives the weight of these water molecules, and the seventh column the total weight of the elements represented as so hydrated. The eighth column gives the reciprocals of the square-roots of these "hydrated weight" values, multiplied by 10^4 for convenience in manipulation. The values of the eighth column represent the theoretical velocities under the indicated hydration as derived through the extension of Graham's Law, and have been designated as V_2 values.

The series as above tabulated comprises the elements of the first quarter of the periodic system,—a unique division. These elements are hereinafter arbitrarily termed the *lighter* elements as distinguished from the remaining heavier elements of the periodic system.

We may study the possible usefulness of Table 1 by using the second assumption of the paper in connection with it,—namely, the assumption that a regular change in weight accompanies ionization. Under such an assumption the most natural increment of change is that which would be effected by the gain or loss of a unit electrical charge on the nucleus of an atom, by virtue of which the weight characteristic represented in column three of Table 1 would be subject to unit change. There are objections to the assumption of a change in weight as an accompaniment of ionization. These objections do not appear to be as serious at present as they would have been before the advent of an electrical interpretation of matter and a knowledge of the modifications characterizing radioactive elements. Nevertheless, the objections to the second assumption may be sustained throughout the inquiry,—notwithstanding which it will be of interest to examine some of the relationships which appear to follow the assumption.

With specific reference to the potassium and sodium ions, K^+ and Na^+, it follows from the above assumption that the regular weight values assigned to the elements, potassium (38) and sodium (22), in

the consideration of their hydration as indicated by relative velocity now become subject to further description as relative weights of the un-ionized or "neutral" elements. These weights as assigned to potassium and sodium further become subject to unit modification for unit charge characterizing the ionized state, and since the potassium and sodium ions being considered have a single positive charge each, it follows that the weights of the so-called "neutral" elements would advance one step upon becoming so ionized. The weight values representing the potassium and sodium ions thus become $K^+ = 40$ and $Na^+ = 24$, and the hydration characterizing these ions as derived from Table 1 is now to be noted as 3 H_2O with K^+ instead of 4 H_2O and 11 H_2O with Na^+ instead of 12 H_2O, the values 4 H_2O and 12 H_2O still representing the indicated degree of hydration characterizing ions of weight 38 and 22 respectively. We now have the K and Na ions with weights modified from the regular values tentatively assigned as prerequisites of an inverse integral hydration relationship and subsequently described as the relative weights of the un-ionized or "neutral" atoms. These modified weights may be further designated as the relative weights of the anhydrous ions, or as "ionic" weights. If the anhydrous ions thus characterized by weight hydrate to the degree corresponding to such a weight, as derived from observed conductivities and indicated in Table 1, it follows that we are now in a position to study the relationship which would have to follow such a hydration system. On the other hand, if the anhydrous ions thus characterized by weight do not hydrate at all, but remain as unhydrated solute ions, it follows that we are also in a position to study the relationships which would have to follow that system. In other words, although we are interesting ourselves primarily in a hydration relationship, we are nevertheless in a strategic position to note an absence of hydration, should any solute ions appear from other considerations to be so characterized.

Before taking up the examination of observed measurements in relation to the two fundamental assumptions of this paper and to the hydration system embodied in Table 1 it may be to our advantage to recapitulate with respect to the use of the word "weight." Our first assumption of an inverse integral hydration required a regular system of weight values. Since the observed *combining weights* did not afford such a system the atomic numbers were doubled to obtain a tentative series of weight values later designated as the relative weights of the un-ionized or "neutral" atoms. Our second assumption of an orderly

change in weight accompanying ionization gave us new values designated as relative weights of the ions, or "ionic" weights. It is to be noted that neither the weights of the "neutral" atoms nor the weights of the ions correspond to the weights characterizing the atoms in combination and commonly designated as the combining weights of the atoms, or more simply, the atomic weights. The possible interrelations of the three designations of weight will be considered at a subsequent point.

We may now turn our attention to the study of the possible usefulness of Table 1 in the prediction of solution characteristics. It immediately becomes evident that in the event the indicated numbers of water molecules combine with the respective element-ions to form hydrated ions, the transfer of such water from the solvent to the solute must profoundly influence the concentration of ions thus hydrated. Jones and his co-workers recognized this fact, but they were without a tentative basis for evaluating the extent of the influence. Table 1 affords such a basis.

The molecular weight values of the hydrated ions of the lighter elements may be readily derived from column seven of Table 1. For example, the molecular weight of the ion K^+ when hydrated may be derived as follows:

$$K = 38,\ K^+ = 38 + 2 = 40,\ K^+ \text{ hydrated} = K^+ + 3\ H_2O = K^+ + (3 \times 18) = 94$$

From the summation weights of the ions characterizing a solution of any electrolyte comprising such ions, the extent of the influence of the assumed hydration may be mathematically calculated. For example, the relative amounts of solvent and solute characterizing a 1.0 molecular solution of KCl would be derived as follows:

$K = 38$, $K^+ = 40$, K^+ hydrated = K^+ (40 gms.) + 3 H_2O (54 gms.) = hydrated K^+, 94 gms.

$Cl = 34$, $Cl^- = 32$, Cl^- hydrated = Cl^- (32 gms.) + 7 H_2O (126 gms.) = hydrated Cl^-, 158 gms.

94 gms. hydrated K^+ + 158 gms. hydrated Cl^- = 252 gms. solute.

In a solution 1.0 molecular made up to 1000 grams, the amount of solvent present would be calculated as 1000 − 252 = 748 gms., or 74.8% of the amount present at "zero" concentration of solute. In a solution 1.0 molecular made up to a liter with observed combining

weights the concentration would be 1.035 on the above basis by virtue of an observed weight of 74.553 as compared with a calculation weight of 72. Moreover, the total weight of solution under the observed conditions would not be 1000 grams, since the density of the solution is not that of the solvent. Yet a relationship between combining weights and the assumed weights for "neutral" and "ionized" atoms can not be considered in this paper without involving argument in digression. Furthermore, in some electrical conductivities of concentrated solutions as observed by various investigators the values have been transposed from a volume to a weight basis through "corrections."[4] Under the circumstances in a reconnaissance survey of certain relationships which appear to follow our initial assumptions we may disregard the factors which differentiate the two bases, and entertain a degree of tolerance for approximate agreements.

Through the use of Table 1, then, we have calculated that at 1.0 molecular concentration a solution of KCl contains 74.8% of the weight of solvent which characterizes it at "zero" concentration. The observed specific molecular conductivities of KCl at "zero" and 1.0 molecular concentrations, 18°C., as given by Noyes and Falk,[5] are 130.0 and 96.5 respectively. The relative specific molecular conductivity is thus 96.5 ÷ 130.0 = .742, or 74.2%.

The obvious suggestion following the order of agreement noted is that the decrease in specific molecular conductivity with concentration, which is quite generally interpreted as indicating incomplete dissociation of the electrolyte, may in reality be an index of the relative weight of solvent present in a solution of a completely ionized electrolyte.

Yet with respect to observed conductivity measurements such an interpretation leads to the inference that the values for concentration, ranging from 1.0 molecular to "zero" molecular, for example, would involve the use of varying bases. If such should prove to be the case the order of relative specific molecular conductivities of various electrolytes comprising ions of the lighter elements should be predictable from the summations of velocities as given in Table 1, through modification to the extent indicated by the summations of weight values (also given in Table 1) in relation to the amount of solvent present. Thus, the amount of solvent characterizing a 1.0 molecular solution of KCl was calculated above from Table 1, as 74.8%. The summation

[4] For example, see Noyes and Falk. Journ. Amer. Chem. Soc., 34: 454, 1912.
[5] Previous citation.

TABLE 2.—Comparison of Observed Specific Molecular Electrical Conductivities of some Electrolytes involving Ions of the Lighter Elements with Velocity, Hydration and Weight Considerations embodied in Table I.

Electrolyte	Observed Weight of Variant Ion of Series	Assumed Weight of Anhydrous Ions (From Table 1)	Assumed Hydration of Ions (From Table 1)	Assumed Weight of Hydrated Ions (From Table 1)	Calculation[6] for % Solvent at 1.0 mol. Concentration	Assumed Relative Velocity of Hydrated Ions (From Table 1)	Calculation for unit molecular Velocity	Calculated Relative Unit Velocity at 1.0 mol. conc.	Observed[7] Relative Unit sp. Mol. Cond. at 1.0 mol. conc.	Calculated Relative % Solvent present at 1.0 mol. conc.	Observed[6] Relative Sp. Mol. Conductivity at 1.0 mol. conc.
LiCl	6.94	$Li^+ = 8$ (comb. wt. = 7) $Cl^- = 32$ (comb. wt. = 33)	$Li^+ = 19\ H_2O$ $Cl^- = 7\ H_2O$ Total = 26 H_2O	$Li^+ = 350$ $Cl^- = 158$ Total = 508	508 − 40 = 468 1000 − 468 = 532 532 ÷ 1000 = .532, or 53.2%	$Li^+ = 535$ $Cl^- = 796$ Total= 1331	.532 × 1331 =708	708	762	53.2	60.7
NaCl	22.997	$Na^+ = 24$ (comb. wt. = 23) $Cl^- = 32$ (comb. wt. = 33)	$Na^+ = 11\ H_2O$ $Cl^- = 7\ H_2O$ Total = 18 H_2O	$Na^+ = 222$ $Cl^- = 158$ Total = 380	380 − 56 = 324 1000 − 324 = 676 676 ÷ 1000 = .676, or 67.6%	$Na^+ = 671$ $Cl^- = 796$ Total = 1467	.676 × 1467 = 992	992	988	67.6	67.8
$MgCl_2$	24.32	$Mg^{++} = 28$ (comb. wt. = 26) $Cl^- = 32$ (comb. wt. = 33)	$Mg^{++} = 9\ H_2O$ $Cl^- = 7\ H_2O$ $Cl^- = 7\ H_2O$ Total = 23 H_2O	$Mg^{++} = 190$ $Cl^- = 158$ $Cl^- = 158$ Total = 506	1000 − 506 = 494 494 ÷ 1000 = .494, or 49.4%	$Mg^{++} = 726$ $Cl^- = 796$ Total = 1522	506 ÷ 2 = 253 1000 − 253 = 747 747 ÷ 1000 = .747 .747 × 1522 = 1137.5	1137.5	1254	49.4	48.7
$AlCl_3$	26.97	$Al^{+++} = 32$ (comb. wt. = 29) $Cl^- = 32$ (comb. wt. = 33)	$Al^{+++} = 7\ H_2O$ $Cl^- = 7\ H_2O$ $Cl^- = 7\ H_2O$ $Cl^- = 7\ H_2O$ Total = 28 H_2O	$Al^{+++} = 158$ $Cl^- = 158$ $Cl^- = 158$ $Cl^- = 158$ Total = 632	1000 − 632 = 368 368 ÷ 1000 = .368, or 36.8%	$Al^{+++} = 796$ $Cl^- = 796$ Total = 1592	632 ÷ 3 = 210.66 1000 − 210.66 = 789.3 789.3 ÷ 1000 = .789 .789 × 1592 = 1256	1256	1288	36.8	36.4
KCl	39.096	$K^+ = 40$ (comb. wt. = 39) $Cl^- = 32$ (comb. wt. = 33)	$K^+ = 3\ H_2O$ $Cl^- = 7\ H_2O$ Total = 10 H_2O	$K^+ = 94$ $Cl^- = 158$ Total = 252	1000 − 252 = 748 748 ÷ 1000 = .748, or 74.8%	$K^+ = 1031$ $Cl^- = 796$ Total = 1827	.748 × 1827 = 1367	1367	1367 (base)	74.8	74.2
$CaCl_2$	40.07	$Ca^{++} = 44$ (comb. wt. = 42) $Cl^- = 32$ (comb. wt. = 33)	$Ca^{++} = 1\ H_2O$ $Cl^- = 7\ H_2O$ $Cl^- = 7\ H_2O$ Total = 15 H_2O	$Ca^{++} = 62$ $Cl^- = 158$ $Cl^- = 158$ Total = 378	1000 − 378 = 622 622 ÷ 1000 = .622, or 62.2%	$Ca^{++} = 1271$ $Cl^- = 796$ Total = 2067	378 ÷ 2 = 189 1000 − 189 = 811 811 ÷ 1000 = .811 .811 × 2067 = 1675	1675	1570	62.2	61.2
KF	19.0	$K^+ = 40$ (comb. wt. = 39) $F^- = 16$ (comb. wt. = 17)	$K^+ = 3\ H_2O$ $F^- = 15\ H_2O$ Total = 18 H_2O	$K^+ = 94$ $F^- = 286$ Total = 380	380 − 56 = 324 1000 − 324 = 676 676 ÷ 1000 = .676, or 67.6%	$K^+ = 1031$ $F^- = 591$ Total = 1622	.676 × 1622 = 1097	1097	1057	67.6	68.35
KCl	35.457	$K^+ = 40$ (comb. wt. = 39) $Cl^- = 32$ (comb. wt. = 33)	$K^+ = 3\ H_2O$ $Cl^- = 7\ H_2O$ Total = 10 H_2O	$K^+ = 94$ $Cl^- = 158$ Total = 252	1000 − 252 = 748 748 ÷ 1000 = .748, or 74.8%	$K^+ = 1031$ $Cl^- = 796$ Total = 1827	.748 × 1827 = 1367	1367	1367 (base)	74.8	75.5

of the velocity values corresponding to the molecular weights of the hydrated ions K and Cl may be derived from Table 1, column 8, as follows:

$$K = 38,\ K^+ = 40,\ K^+ \text{ hydrated} = 40 + 3\ H_2O,\ V_2 = 1031$$
$$Cl = 34,\ Cl^- = 32,\ Cl^- \text{ hydrated} = 32 + 7\ H_2O,\ V_2 = 796$$
$$\text{Summation} = 1827$$

If, now, we represent the specific molecular conductivity of KCl at "zero" concentration by the summation velocity value 1827, at 1.0 molecular concentration the apparent relative velocity value may be calculated as 74.8% of 1827, or 1367, since the transfer of water from solvent to solute under the assumed inverse integral hydration system would reduce the apparent concentration of solvent, as previously noted.

We may now examine a group of electrolytes involving ions of the lighter elements with respect to the above suggestions and the assumed interrelations of weight, hydration and velocity embodied in Table 1. To facilitate such an examination the respective data are brought together in Table 2.

In Table 2, the electrolytes in the respective series are arranged in the order of the increasing atomic weight of the variant ion, as indicated in the second column. In such series the assumption of an inverse integral relationship between weight and hydration would yield relative velocities of an order increasing with weight as calculated

[6] Observed values may involve weight-normal or volume-normal solutions. The observed values cited for LiCl, NaCl and KF involved no "correction" to weight-normal basis, and calculations are, therefore, made to correspond with the observed volume-normal basis. The other observed values involve "corrections" to the weight-normal basis. All observed values in the first series are at 0°C., and in second series at 18°C., except as otherwise noted.

[7] LiCl, Jones and Getman, Ztschr. phys. Chem. 46, 1903, p. 262, 1.67 m = 42.28, .88 m = 35.58, by interpolation 1.0 mol. = 36.597; NaCl, Int. Crit. Tables, Vol. VI, p. 233, 1.0 mol. = 47.5; $MgCl_2$, Jones, Carn. Inst. Wash. Pub. 180, p. 65, .9415 m = 60.31; $AlCl_3$ same p. 78, 1.0 mol. = 61.93; KCl, same p. 16, 1.05 mol. = 65.7; $CaCl_2$ same, p. 16, 1.0 mol. = 75.5; KF, Noyes and Falk, J. A. Chem. Soc. 34, 1912, p. 463, 1.0 mol. = 75.95; KCl, same, p. 463, 1.0 mol. = 98.22.

[8] Additional values as follows: LiCl, Washburn, J. A. Chem. Soc. 33, 1911, p. 1474, "zero" conc. = 60.3; NaCl, Kohlrausch and Holborn, Leitvermögen der Elektrolyte, 1898, p. 158 [18°C.], 1.0 mol. = 74.4, .0001 mol. = 109.7; $MgCl_2$, Jones, Carn. Inst. Wash. Pub. 180, p. 65, "zero" conc. = 123.95; $AlCl_3$, same, p. 78, "zero" conc. = 170; KCl, Noyes and Falk [18°C.], J. A. Chem. Soc. 34, 1912, p. 461, "zero" conc. = 130.0, p. 462, 1.0 mol. conc. = 96.5; $CaCl_2$, Jones, Carn. Inst. Wash. Pub. 180, p. 63, "zero" conc. = 123.46; KF, Noyes and Falk, J. Am. Chem. Soc. 34, 1912, p. 461, "zero" conc. = 111.2.

from Table 1 and given in the ninth column. The observed velocities as inferred from the relative unit specific molecular conductivities given in the tenth column are to be noted as of corresponding order. On the other hand, the specific hydration values derived from the above assumption as related to the observed relative ion conductance of the Na and K ions yield an entirely random series of values for the amount of solvent characterizing 1.0 molecular solutions of the respective electrolytes as derived in the fifth and sixth columns and given in the seventh column. The observed relative specific molecular conductivities at 1.0 molecular concentration given in the twelfth column are to be noted as of a corresponding order. In the last four columns of Table 2 we have, therefore, a double-checking series of comparisons relating the values of Table 1 to observed measurements. On the one hand relative velocities predicted upon the assumed hydration through the extension of Graham's Law are to be noted as in substantial agreement with observed relative conductivities. On the other hand, the changes in concentration of solvent which would be anticipated from the assumed hydration are to be noted as in agreement with the observed apparent modifications of specific molecular conductivities. These interlocking series of comparisons involving two aspects of solution phenomena as measured by electrical conductivity thus appear to be characterized by agreements beyond the possibility of mere accident.

In the third column of Table 2, it may be noted that assumed combining weights are given in parentheses below the assumed weights of the anhydrous ions. These combining weights are intermediate between the respective "neutral" and "ionic" weights previously discussed, and mathematically represent the sharing of electrons in chemical combination, considered from the standpoint of weight-change as an accompaniment of ionization. For example, if the element sodium represented as Na is assigned a weight of 22 in the un-ionized or "neutral" state, and a weight of 24 following the loss of an electron to become positively ionized as Na^+, then when it shares a single electron in combination, its combining weight quite naturally may be assumed as the intermediate value, or 23. The values thereby attained as combining weights for such ions as Li^+, Na^+ and K^+ do not depart appreciably from observed values, but since the corresponding values for many other ions are at variance with observed values the matter of combining weights of the lighter elements requires particular consideration in relation to the assumptions regarding hydration and weight change. If we are to make the two

initial assumptions of this paper it appears incumbent upon us to eventually define combining weight and relate it to a substantial group of observed measurements. At this time, however, the matter of the hydration of the ions must take precedence, and their combining weights must remain parenthetical.

We may now continue the inquiry through an examination of the measurements of other phases of solution phenomena.

Freezing-Point Depression as an Index of Hydration in the Lighter Element Ions

The work of Raoult[9] established an importance for the freezing-point depression of a solvent effected by a solute, and in subsequent years the measurement has become important in the determination of the molecular weights of dissolved non-electrolytes, in the measurement of osmotic pressure of both electrolytes and non-electrolytes and in the measurement of the electrolytic dissociation of electrolytes. As related to each of these applications the usefulness of the measurement appears to be largely restricted to dilute solutions. As related to osmotic pressure the measurement has attained importance through analogy, following the demonstration of a direct proportionality between freezing-point lowering and osmotic pressure. As related to the electrolytic dissociation of electrolytes the measurement attained importance through inference, following the interpretation of the decrease in specific molecular conductivity with increase in concentration as an index of incomplete dissociation.

Yet in the foregoing section observed electrical conductivity values for solutions involving ions of the lighter elements were noted as corresponding with hydration, weight and velocity values predictable from Table 1. The apparent decrease in observed specific molecular electrical conductivity with increase in concentration was suggested as associated with unevaluated changes in concentration caused by the hydration of the ions. The "true" specific molecular conductivity was thus indicated as a constant, whereupon complete ionization at all concentrations became characteristic of all solutions under the initial assumptions of the paper. It will be of interest to study the freezing-point depression of electrolytes involving the lighter element-ions with respect to the considerations embodied in Table 1.

In dilute solutions the depression of the freezing-point of the solvent by the solute is considered proportional to the number of molecules or ions of solute present.

[9] Ann. Chem. Phys. **28**: 137, 1883; **2**, 66, 1884.

We may now examine some observed freezing-point depressions with particular reference to the familiar relationship underlying the interpretation of freezing-point data, namely, that the gram molecular weight of a non-ionizing solute added to 1000 gms. of water reduces the freezing-point by 1.86°C. This relationship is considered as subject to direct modification through ionization, a solute giving rise to two ions, as KCl, effecting a reduction of 2 × 1.86°C., or 3.72°C. and a solute giving rise to three ions, as $CaCl_2$, effecting a reduction of 3 × 1.86°C., or 5.58°C. The degree of agreement between the values postulated under such a relationship and the observed values is commonly interpreted as a measure of dissociation. Yet under the assumptions of this paper electrical conductivities suggest complete ionization at concentrations up to 1.0 molecular KCl or its ionic equivalent.

TWO-ION ELECTROLYTES

Lithium Chloride, LiCl: The following observed values for the freezing-point depression of this electrolyte may be cited:[10] 1.0 mol. = 3.80°; .7939 mol. = 2.945°; .5012 mol. = 1.81°; .2474 = 0.86°. The summation weight representing the hydrated solute LiCl at 1.0 mol. concentration as derived from Table 1 is 508, and the proportionate values of the above concentrations may be calculated as follows: 1.0 mol. = 1 × 508 = 508; .7939 mol. = .7939 × 508 = 403.5; .5012 mol. = .5012 × 508 = 254.7; .2474 mol. = .2474 × 508 = 125.8. The observed freezing-point depressions are plotted against these proportionate values in the graph shown in Figure 1 and connected by a heavy line. For comparison we may venture to indicate the freezing-point depression of LiCl when the complete ionization suggested by electrical conductivity measurements is assumed. This depression would be 2 × 1.86°C. (unit molecular depression), or 3.72°C. for a summation weight of an electrolyte forming two ions. The weight value, 508, represents the amount of solute at 1.0 molecular concentration. The values are represented in the graph shown in Figure 1 as a broken line.

Sodium Chloride, NaCl. The following observed values for the freezing-point depression of this electrolyte may be cited:[11] 1.0 mol. = 3.37°; .700 mol. = 2.4°; .4293 mol. = 1.447°; .2325 mol. = .796°.

[10] 1.0 mol. from Int. Crit. Tables, 4: 258. Other values from page 227 in Smithsonian Tables, 6th Edition, 1914.

[11] 1.0 mol. from Int. Crit. Tables, 4: 258. Other values from page 227 in Smithsonian Tables, 6th Edition, 1914.

The summation weight representing the hydrated solute, NaCl, at 1.0 mol. concentration as derived from Table 1 is 380, and the proportionate values of the above concentrations may be calculated as follows: 1.0 mol. = 1 × 380 = 380; .700 mol. = .700 × 380 = 266; .4293 mol. = .4293 × 380 = 163.2; .2325 mol. = .2325 × 380 = 88.4. The observed freezing-point depressions are plotted against these proportionate values in the graph shown in Figure 1 and connected by a heavy line. The calculated depression for the ionization Na^+

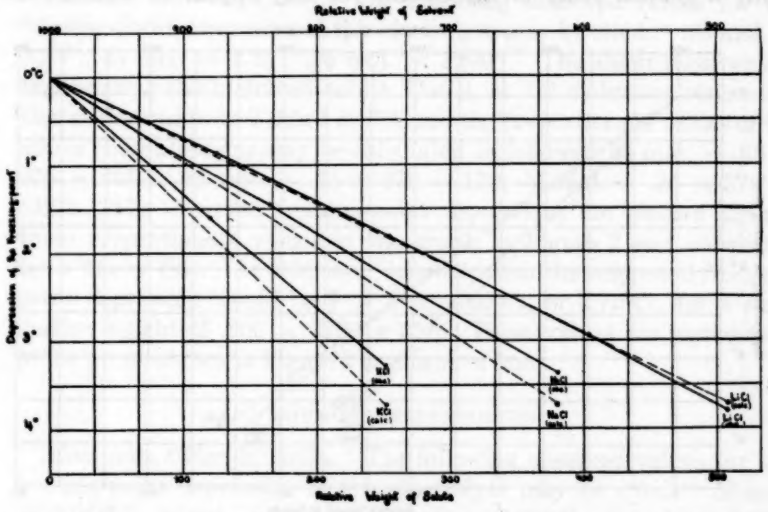


Fig. 1. Observed and calculated freezing-point depressions for some two-ion electrolytes.

and Cl^- would be 2 × 1.86°C., or 3.72°C. for a summation weight of 380, representing the amount of solute present at 1.0 molecular concentration. The values are represented in the graph shown in Figure 2 as a broken line.

Potassium Chloride, KCl. The following observed values for the freezing-point depression of this electrolyte may be cited:[12] 1.0 mol. = 3.268°; .476 mol. = 1.605; .3139 mol. = 1.07. The summation weight representing the hydrated solute KCl at 1.0 mol. concentration as derived from Table 1 is 252, and the proportionate values of the above concentrations may be calculated as follows: 1.0 mol. = 1 × 252 = 252; .476 mol. = .476 × 252 = 120; .3139 mol. = .3139 ×

[12] Smithsonian Tables, 6th Edition, p. 227, 1914.

252 = 79.2. The observed freezing-point depressions are plotted against these proportionate values in the graph shown in Figure 1 and connected by a heavy line. The calculated depression for the ionization K^+ and Cl^- would be $2 \times 1.86°C.$, or 3.72°C. for a summation weight of 252, representing the amount of solute present at 1.0 molecular concentration. The values are represented in the graph shown in Figure 1 as a dotted line.

The comparisons set forth in the graph shown in Figure 1 indicate only a general order of agreement, yet they appear to warrant the

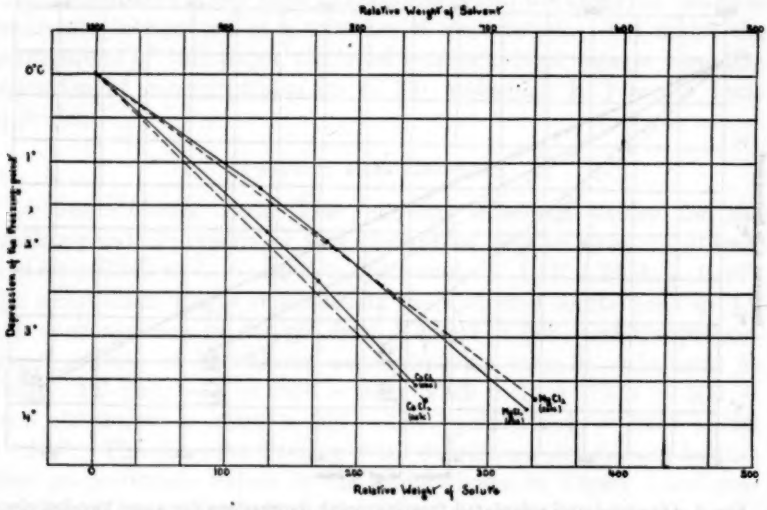


Fig. 2. Observed and calculated freezing-point depressions for some three-ion electrolytes.

consideration of other electrolytes at corresponding ionic concentrations.

THREE-ION ELECTROLYTES

Magnesium Chloride, $MgCl_2$. The following observed values for the freezing-point depression of this electrolyte may be cited.[13] .65 mol. = 3.854; .45 mol. = 2.537; .35 mol. = 1.910; .25 mol. = 1.306. The summation weight representing the hydrated solute $MgCl_2$ at 1.0 molecular concentration as derived from Table 1 is 506, and the proportionate values of the above concentrations may be calculated

[13] Jones, H. C. Carn. Inst. Wash. Pub. 180: 23, 1913.

as follows: .65 mol. = .65 × 506 = 329; .45 mol. = .45 × 506 = 228; .35 mol. = .35 × 506 = 177; .25 mol. = .25 × 506 = 126.5. The observed freezing-point depressions are plotted against these proportionate values in the graph shown in Figure 2 and connected by a heavy line. At .666 mol. concentration, equi-ionic with 1.0 molecular KCl, the calculated freezing-point depression would be $\frac{2}{3} \times 3 \times 1.86°C. = 3.72°C.$, for a summation weight of .666 × 506, or 337. These values are represented in the graph as a broken line.

Calcium Chloride, $CaCl_2$. The following observed values for the freezing-point depression of this electrolyte may be cited:[14] .65 mol. = 3.55°; .45 mol. = 2.35°; .35 mol. = 1.801°. The summation weight representing the hydrated solute, $CaCl_2$, at 1.0 molecular concentration as derived from Table 1 is 378, and the proportionate values of the above concentrations may be calculated as follows: .65 mol. = .65 × 378 = 245.8; .45 mol. = .45 × 378 = 170; .35 mol. = .35 × 378 = 132.3. The observed freezing-point depressions are plotted against these proportionate values in the graph in Figure 2 and connected by a heavy line. At .666 mol. concentration the suggested freezing-point depression would be $\frac{2}{3} \times 3 \times 1.86°C.$, or 3.72°C., for a summation weight of .666 × 378, or 252. These values are represented in the graph shown in Figure 2 as a broken line.

FOUR-ION ELECTROLYTE

Aluminum Chloride, $AlCl_3$. The following observed values for the freezing-point depression of this electrolyte may be cited:[15] .50 mol. = 3.9446°; .4 mol. = 2.910; .25 mol. = 1.6604°; .2 mol. = 1.279. The summation weight representing the hydrated solute $AlCl_3$ at 1.0 molecular concentration as derived from Table 1 is 632, and the proportionate values of the above concentrations may be calculated as follows: .50 mol. = .50 × 632 = 316; .4 mol. = .4 × 632 = 252.8; .25 mol. = .25 × 632 = 158; .2 mol. = .2 × 632 = 126.4. The observed freezing-point depressions are plotted against these proportionate values in the graph shown in Figure 3 and connected by a heavy line. At .50 molecular concentration, equi-ionic with 1.0 molecular KCl, the calculated freezing-point depression would be $\frac{1}{2} \times 4 \times 1.86°C.$, or 3.72°, for a summation weight of $\frac{1}{2} \times 632$, or 316. These values are represented in the same graph as a dotted line.

The order of agreement to be noted in the foregoing graphs indicates

[14] Jones, H. C. Carn. Inst. Wash. Pub. **180**: 22, 1913.
[15] Jones, H. C. Carn. Inst. Wash. Pub. **180**: 78, 46, 1913.

that the suggestion of complete ionization at concentrations as great as 1.0 molecular, a suggestion arising from a consideration of electrical conductivity measurements, is not without support in the data of freezing-point determinations. It is readily apparent that at the lower concentrations shown in the graphs the observed freezing-point depressions are less than the calculated values. These differences are substantially off-set when the concentrations of the observed values are recalculated on the weight-normal basis used in apportioning the relative amounts of solute and solvent. It is further apparent from

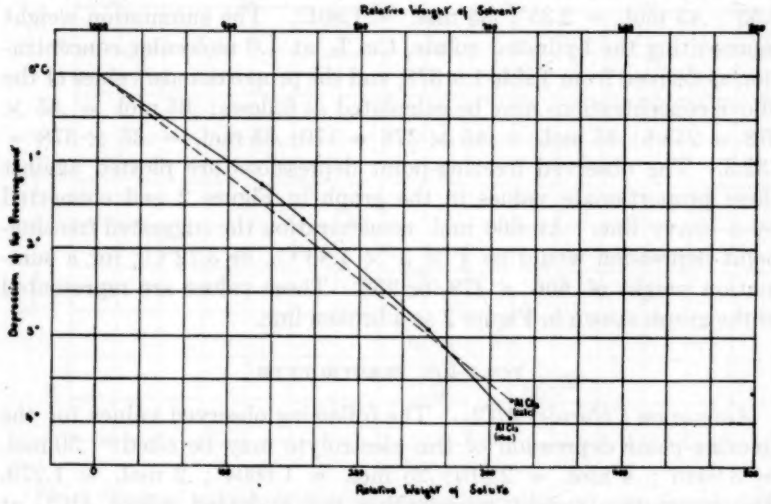


Fig. 3. Observed and calculated freezing-point depressions for a four-ion electrolyte

these graphs, moreover, that at concentrations approaching one molecular (for KCl type), or its ionic equivalent, the observed freezing-point depressions of such electrolytes as LiCl, $MgCl_2$ and $AlCl_3$ are greater than those anticipated under the calculated straight-line relationship. These electrolytes are indicated in Table 2 as being characterized by the greater degree of hydration, suggested as a significant factor in the more concentrated solutions. It appears to be of interest, therefore, to examine the freezing-point measurement to the point of solidification of the solution.

A series of freezing-point measurements of solutions of $CaCl_2$ at various concentrations approaching the point at which the solution

solidifies are available from Jones,[16] and on this account this electrolyte will be examined in some detail with respect to hydration.

As derived from Table 1 the anhydrous calcium ion, Ca^{++}, has a weight of 44 (suggesting thereby a combining weight of 42), with a hydration of one water molecule, by virtue of which hydration the hydrated ion has a weight of 62. Similarly, the anhydrous chlorine ion, Cl^-, has a weight of 32 (suggesting thereby a combining weight of 33) with a hydration of seven water molecules, the weight of the hydrated ion being 158. On such a basis, therefore, the summation weights associated with $CaCl_2$ are as follows: anhydrous state, Ca^{++} = 44, Cl^- = 32, Cl^- = 32, total = 108; hydrated state, Ca^{++} = 62, Cl^- = 158, Cl^- = 158, total = 378. We may now calculate a series of characteristics for solutions of $CaCl_2$ at various concentrations on the foregoing basis. Taking 1000 grams of solution as a concentration standard, we may calculate the expected saturation point as follows: $1000 \div 378 = 2.645$. At 2.645 molecular on the weight basis the solution should be saturated, and when concentration is expressed as a weight of electrolyte added to 1000 gms. of water, (which is the basis of concentration used in freezing-point depression studies), and the observed weight of $CaCl_2$ is taken as 111, the 2.645 molecular value becomes 3.605 molecular, or 400 grams $CaCl_2$ added to 1000 gms. H_2O. The expected depression of the freezing-point at 2.645 molecular, assuming complete ionization, may be calculated as follows: $2.645 \times 3 \times 1.86° = 14.76°$. But whereas at zero concentration of solute there are 1000 grams of free solvent and anhydrous solute present, at 2.645 molecular concentration of solute there is no free solvent present and 286 gms. of solute. If the freezing-point depression is assumed to have been influenced by this change, the extent of the influence becomes measurable by simple division, in which the relative amount of solvent and anhydrous solute is expressed as a fraction. Thus $14.76° \div .286 = 51.6°$. On such a basis, therefore, we may calculate the expected additional depression of the freezing-point attributable to the transfer of water from solvent to solute under the assumed hydration. A series of values for $CaCl_2$ at various concentrations has been calculated and incorporated in Table 3, wherein is also cited a series of corresponding values from observed freezing-point depressions at various concentrations as obtained by Jones.

[16] Jones, H. C. Carn. Inst. Wash. Pub. 180: 15, 1913.

We may now plot the values of Table 3 relating to proportion of solute and freezing-point depression. In the graph in Figure 4 calculated values appear represented by heavy lines. The straight line is derived from column four of the calculated series, and is an expression of the relationship fundamental to the interpretation of freezing-point depression—1.86°C. depression for each gram ion

TABLE 3.—DATA OF CALCULATED AND OBSERVED FREEZING-POINT DEPRESSION IN RELATION TO AN ASSUMED HYDRATION

Mol. Conc. (Observed Basis)	Grams Hydrated Solute	Conc. Hydrated Solute (Weight Basis)	Calc. Freezing-Point Depression (Conc. Hyd. Sol. × 3 × 1.86°)	Grams Free Solvent	Grams Anhydrous Solute	Grams Solvent Plus Grams Anhydrous Solute	Freezing-Point Depression Calculated for conc. on Observed Basis,	
CALCULATED SERIES								
0	0	0	0°	1000	0	1000.	0°	
.5	184	.487	2.72°	816	52.6	868.6	3.13°	
1.0	350	.926	5.165°	650	100.	750.	6.89°	
1.5	500	1.323	7.38°	500	142.75	642.75	11.48°	
2.0	636	1.6825	9.385°	364	181.8	545.8	17.22°	
2.5	760	2.01	11.22°	240	217.3	457.3	24.52°	
3.0	876	2.318	12.93°	124	250.	374.	34.58°	
3.5	980	2.592	14.475°	20	280.	300.	48.25°	
3.605	1000	2.645	14.76°	0	286.	286.	51.6°	
OBSERVED SERIES								
								Obs. Δ
.3	113	.299	1.67°	887	32.3	919.3	1.82°	1.517°
.7	253	.67	3.74°	747	72.2	819.2	4.57°	4.065°
1.0	350	.926	5.16°	650	100.	750.	6.88°	6.41°
1.4	471	1.246	6.95°	529	134.5	663.5	10.48°	10.05°
1.75	569	1.505	8.40°	431	162.6	593.6	14.17°	14.33°
2.2	687	1.8175	10.15°	313	196.3	509.3	19.95°	21.07°
2.7	808	2.138	11.92°	192	232.	424.	28.1°	30.25°
3.1	896	2.37	13.23°	104	256.	360.	36.75°	39.5°
3.51	980	2.59	14.45°	20	280.	300.	48.15°	49.5°

present—although the concentration basis has been modified from "a weight of electrolyte added to 1000 gms. water" to "a weight of electrolyte in 1000 gms. solution." This fundamental relationship thus involves the number of ions present, and in so doing further involves the implication that all solute ions are of the same size—an implication which also follows from the extension of the gas laws in relation to velocity as interpreted through observed electrical conductivities. The curved line derived from column eight of the same

series is an expression of the modification of the straight-line relationship which might be anticipated as a result of the assumed hydration. In other words, under the assumed hydration each molecule of $CaCl_2$ removes fifteen water molecules of solvent, and the unevaluated concentration thereby brought about gives an apparent falling-off in freezing-point depression represented by the departure of the curved line from the straight line.

We may now examine the values for freezing-point depression as derived from column nine of the observed series and represented by a dotted line curve in the graph.

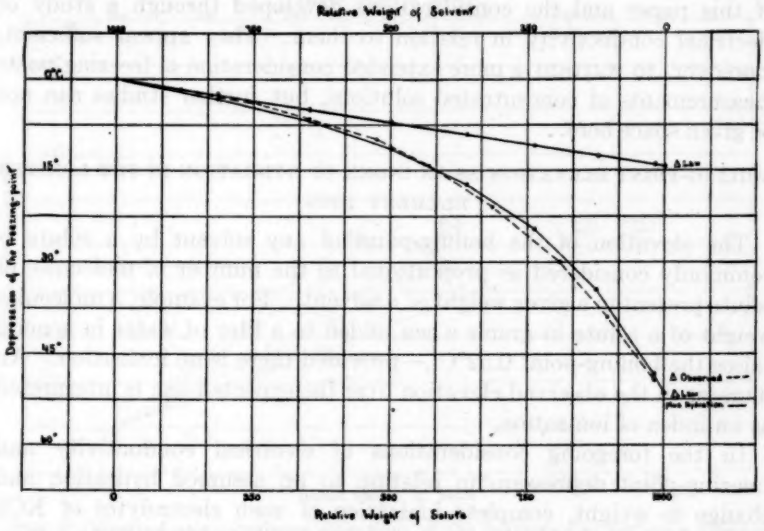


Fig. 4. Observed and calculated freezing-point depressions for aqueous solutions of $CaCl_2$ at all concentrations.

The agreement between the observed and calculated values as represented respectively by the dotted and full curved lines appears to be beyond the possibility of accident. The calculated point at which the mixture of $CaCl_2$ and water becomes 100% hydrated $CaCl_2$ (-51.6°C.) corresponds with the observed cryohydric or eutectic point for $CaCl_2$ in water,[17] which agreement further substantiates the specific hydration assumed. It is of interest to note also that the concentration indicated by the depression 51.6° is 9.25 mol. ($51.6 \div 5.58 = 9.25$). This concentration has the same rela-

[17] Int. Crit. Tables, 4: 257, gives -51°C.

tionship to the concentration of hydrated solute, 2.645 mol., as does the initial weight of solvent (1000) to the final weight of anhydrous solute at saturation (286). Since the molecular weight of $CaCl_2$ is involved in the foregoing relationships it is obvious that these freezing-point depression measurements may serve as indices of the weights of calcium and chlorine, the assumed weights being at variance with those commonly observed. As previously noted the matter of combining weight can not be considered in this paper.

The order of agreements above noted with respect to the depression of the freezing-point appears to be in support of the initial assumptions of this paper and the considerations developed through a study of electrical conductivity in relation to them. They appear sufficient, moreover, to warrant a more extended consideration of freezing-point measurements of concentrated solutions, but further studies can not be given space here.

BOILING-POINT ELEVATION AS AN INDEX OF HYDRATION IN THE LIGHTER ELEMENT IONS

The elevation of the boiling-point of any solvent by a solute is commonly considered as proportional to the number of molecules of solute present in a given weight of a solvent. For example, a molecular weight of a solute in grams when added to a liter of water in general raises the boiling-point 0.52°C.,—provided there is no ionization. An increase in the observed elevation over the expected one is interpreted as an index of ionization.

In the foregoing considerations of electrical conductivity and freezing-point depression in relation to an assumed hydration and change in weight, complete ionization of such electrolytes of KCl, LiCl, $CaCl_2$, etc., has been suggested at all concentrations. Consequently on the above basis we would expect that a gram-molecular-weight of KCl, for example, dissolved in a liter of water, would raise the boiling point twice the unit molecular amount, or 1.04°C. Similarly we would expect that a three-ion electrolyte, as $CaCl_2$, would raise the boiling-point $3 \times .52°$, or 1.56°, while $AlCl_3$ as a four-ion electrolyte would raise the boiling-point 2.08°C.

On the foregoing bases we may compare the calculated and observed elevations of the boiling-point characterizing solutions of electrolytes involving ions of the lighter elements as follows:[18]

[18] References for observed values: KCl, NaCl, Jablczyński and Kon, Jour. Chem. Soc., London **123**: 2953, 1923. $CaCl_2$, Baker and Waite, Chem. and Metallurgical Engineering **25**: 1174, 1921. Mg Cl_2, Kahlenberg, L., Jour. of Physical Chem. **5**: 366, 1901. Li Cl, Biltz, Zeit. fur physik. Chemie, **40**: 208, 1902.

TWO-ION ELECTROLYTES

Calculated KCl: Assuming for an approximation that one mole in 1000 parts by weight effects a unit elevation of .52°C., we have KCl, K^+ = 40, mol. wt. hyd. = 94, Cl^- = 32, mol. wt. hyd. = 158, 94 + 158 = 252, total mol. wt. 2 ions, 2 × .52° = 1.04°; *Observed KCl*: .8842 m. = .824°, .8842 × 252 = 223. *Calculated NaCl*: Na^+ = 24, mol. wt. hyd. = 222, Cl^- = 32, mol. wt. hyd. = 158, 222 + 158 = 380, total mol. wt. 2 ions, 2 × .52° = 1.04°, *Observed NaCl*: .9208 m. = .888°, .9208 × 380 = 350. *Calculated LiCl*: Li^+ = 8, mol. wt.

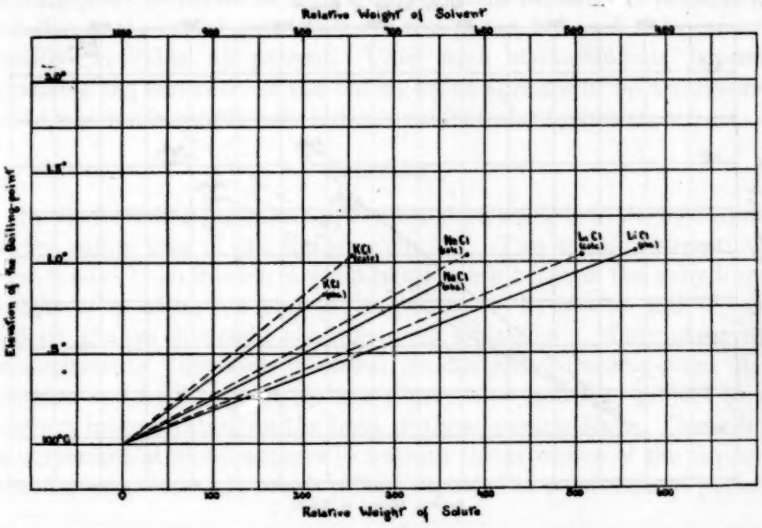


Fig. 5. Observed and calculated elevations of the boiling-point for some two-ion electrolytes.

hyd. = 350, Cl^- = 32, mol. wt. hyd. = 158, 350 + 158 = 508, total mol. wt. hyd. 2 ions, 2 × .52° = 1.04°, *Observed LiCl*: 1.05 m. LiCl gives an elevation of the boiling point of 1.063°C. *Observed Weight* LiCl = 42.48, *Calculated Weight* = 40, 42.48 ÷ 40 = 1.062, 1.062 × 1.05 = 1.115, 1.115 × 508 = 566.

THREE-ION ELECTROLYTES

Calculated $CaCl_2$: Ca^{++} = 44, mol. wt. hyd. = 62, Cl^- = 32, mol. wt. hyd. = 158, Cl^- = 32, mol. wt. hyd. = 158, 62 + 158 + 158 = 378, total mol. wt. 3 ions, 3 × .52° = 1.56°. *Observed $CaCl_2$*: 10 gms. $CaCl_2$ added to 100 gms. H_2O, gives boiling point of 101.3°C. Same

as 100 gms. added to 1 liter H_2O, 100 ÷ 1100 = .091 or 91 parts per thousand. 91 ÷ 108 (theo. mol. wt. anhydrous $CaCl_2$) = 318. Elevation effected: 1.3°C. *Calculated* $MgCl_2$: Mg^{++} = 28, mol. wt. hyd. = 190, Cl^- = 32, mol. wt. hyd. = 158, Cl^- = 32, mol. wt. hyd. = 158, 190 + 158 + 158 = 506, total mol. wt. 3 ions, 3 × .52° = 1.56°. *Observed* $MgCl_2$: 9.156 gms. added to 100 gms. water raised boiling point 1.351°C. Equivalent to 91.56 gms. added to 1000 gms. water. 91.56 : 1091.56 :: x : 1000, x = 73.9 (equivalent to 83.9 gms. per 1000 gms. solution), 83.9 ÷ 92 (mol. wt. anhydrous $MgCl_2$)

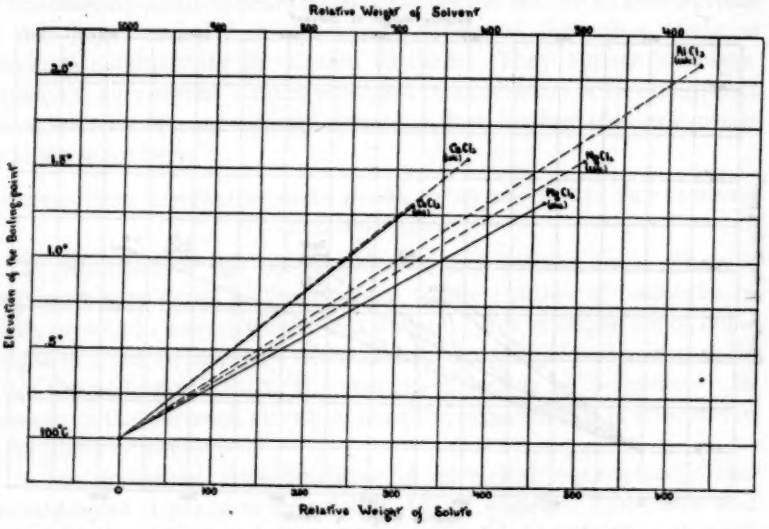


Fig. 6. Observed and calculated elevations of the boiling-point for some electrolytes of more than two ions.

= .912, .912 × 506 (mol. wt. hyd. $MgCl_2$) = 461.5, relative wt. of hydrated solute.

FOUR-ION ELECTROLYTES

Calculated $AlCl_3$: Al^{+++} = 32, mol. wt. hyd. = 158, Cl^- = 32, mol. wt. hyd. = 158, Cl^- = 32, mol. wt. hyd. = 158, Cl^- = 32, mol. wt. hyd. = 158, 158 (Al^{+++}) + 158 (Cl^-) + 158 (Cl^-) + 158 (Cl^-) = 632, 4 ions, 4 × .52° = 2.08°. *Observed* $AlCl_3$: Corresponding observed values are not readily available at this writing.

An examination of the graphs in Figures 5 and 6 indicates that the calculated and observed values are in substantial agreement, and the

boiling-point measurements to the extent of the agreements thus become subject to interpretation as indicating complete ionization at all concentrations. The data thus appear to support the suggestions of electrical conductivity and freezing-point depression in this regard.

With the addition of more and more solute to a solvent the boiling-point is raised higher and higher. The ratios of solvent to solute brought about by such concentrations suggest that the assumed attraction of the solute for the solvent is gradually offset through the elevation of the temperature. In any case the measurement of boiling-point elevation at high concentrations becomes of interest in relation to the initial assumptions of this paper, but such data are not readily available at present. Until such measurements become available the elevation of the boiling-point appears to be a measurement which can supply only indirect evidence for hydration.

Summary

In the foregoing pages an inquiry has been made into the hydration of the solute ions of the lighter elements. Two initial assumptions were made (1) an inverse integral relationship between the anhydrous weight of a solute ion and the degree of its hydration and (2) an orderly change in weight accompanying ionization. Many observed measurements, involving electrical conductivity, freezing-point depression and boiling-point elevation have been noted as subject to a uniform interpretation on the basis of these assumptions. The order of agreement attained appears to warrant the extension of the inquiry to other ions,—a study which will be reported in a subsequent paper.

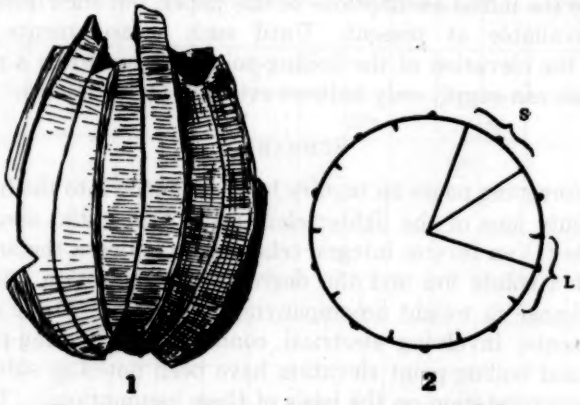
PALEOBOTANY.—*A sterculiaceous fruit from the lower Eocene (?) of Colorado.*[1] Edward W. Berry, Johns Hopkins University.

A unique fossil fruit, which was sent to me for determination some months ago by Professor R. D. George of the University of Colorado, is sufficiently characteristic and important to be placed on record. It seems to be definitely referable to the family Sterculiaceae, which family is abundantly represented by a variety of foliar remains throughout the Upper Cretaceous and early Tertiary, but which becomes restricted to the warmer and more humid regions of lower latitudes after the early Tertiary.

The limited amount of carpological material of recent members of the Sterculiaceae or of allied families of the order Malvales has pre-

[1] Received January 19, 1932.

vented me from finding an exact living representative of the fossil assuming that there is such a representative, and I have therefore been constrained to refer it to the form genus *Sterculiocarpus*. This genus was proposed by me[2] in 1916 for fruits belonging to the family Sterculiaceae, but with unknown or uncertain existing representatives. Two species, *Sterculiocarpus eocenicus*[3] and *Sterculiocarpus sezanelloides*,[4] were described, and a third species, *Sterculiocarpus sphericus*, was described[5] in 1930. These were all from the lower Eocene Wilcox group and clearly represented three distinct types which it is difficult to imagine could have come within the limits of a single natural genus.



Figs. 1, 2.—*Sterculiocarpus coloradensis*, natural size

The only other pertinent reference in the literature is a paper by Viguier[6] describing the remarkable flowers and fruits from the lower Eocene travertine of Sézanne in France, which are definitely referable to the tribe Lasiopetaleae of this family, and for which the genus *Sezanella*, with two species was erected.

The present specimen may be described as follows:

Sterculiocarpus coloradensis n. sp.

Figs. 1, 2.

The single specimen consists of a limonite replacement, whether secondary after siderite, directly from lignite, or a cavity filling is unknown, of a large

[2] EDWARD W. BERRY. U. S. Geol. Survey Prof. Paper **91**: 287. 1916.
[3] *Idem:* 288, pl. 74, figs. 1–3.
[4] *Idem:* 288, pl. 72, figs. 4–6.
[5] E. W. BERRY. U. S. Geol. Survey Prof. Paper **156**: 109, pl. 25, fig. 19; pl. 48, figs. 9–14. 1930.
[6] R. VIGUIER. Revue génér. bot. **20**: 6–13, text fig. 1–6, pl. 5. 1908.

spheroidal capsule. One longitudinal half is nearly complete and there are parts of nearly all of the base of the opposite side.

Form prolate spheroidal, somewhat more fully rounded proximad than distad. Length about 5.25 centimeters. Equatorial diameter about 4 centimeters in the plane of flattening and 3 centimeters in the plane at right angles to it. Surface with 10 fairly prominent longitudinal ridges, equally alternating with 10 sulcae. The latter may be a living feature but have the appearance of representing lines of dehiscence of a tardily dehiscent capsule. The surface is minutely ornamented with fine transverse, subparallel, inosculating, impressed lines, which may be a natural feature, or merely result from the manner of fossilization. Exposed inner faces in the radial planes of the surface sulcae show similar markings, and these are the basis for considering the capsule to have been septicidal.

The capsule is divided into 10 compartments and appears to have been ligneous in life. It is possible that the longitudinal ridges of the outer surface represent the exterior edge of the compartment walls, in which case the dehiscence was loculicidal. The first of these alternatives seems the more probable. It is also possible that these ridges represent the position of parietal placentae, but it seems more likely that the placentation was axile. I surmise this from rather obscure internal markings which may represent the impression scars of seeds. No structural features other than those mentioned are discernable.

An undeformed equatorial cross section is shown in fig. 2 and I have indicated on this the alternative interpretations at **S** (septicidal) and **L** (loculicidal).

The single specimen is the property of Cecil Shelton of Kutch, Colorado, and it came from the valley of Big Sandy Creek in Sec. 5, T. 11 S., R. 60 W., 6th principal meridian. The country rock here is Laramie, near the Laramie-Dawson contact. Tertiary rocks of Miocene-Pliocene age border the valley on both the north and south sides within a couple of miles. It seems probable that the fossil is of Dawson age, although this is subject to the uncertainty attending the discovery of an entirely new type. An early Eocene age is assigned to the Dawson.

The only comparable carpological remains, which have already been mentioned (*ante*) come from the lower Eocene of the Mississippi Gulf embayment, and from the lower Eocene of France, but the weight of this is somewhat discounted by the fact that leaves of various types of Sterculiaceae are common as early as the base of the Upper Cretaceous in this general region, where they disappear after Eocene time. The present specimen, although differing in size and external form, agrees with *Sezanella* in having ten compartments, septicidal dehiscence, and axile placentae.

PROCEEDINGS OF THE ACADEMY AND AFFILIATED SOCIETIES

THE ACADEMY

244TH MEETING

The 244th meeting of the Academy was held in the Auditorium of the Interior Department Building, on Wednesday, December 9, 1931. President

N. A. COBB called the meeting to order at 8:15 and introduced the speaker of the evening, Dr. E. G. CONKLIN, Professor of Zoology, Princeton University, who delivered an illustrated address on *Fitness and purpose in the living world.* About 270 persons were present.

245TH MEETING

The 245th meeting of the Academy was a joint meeting with the Geological Society of Washington, held in the Auditorium of the Interior Department Building, on Tuesday, January 12, 1932. 150 persons were present. Vice-President H. L. CURTIS called the meeting to order at 8:15 and introduced Dr. F. E. MATTHES who presented Professor F. A. VENING MEINESZ of the University of Utrecht, member of the Netherlands Geodetic Commission, who delivered an address on *Gravity results of submarine expeditions in the East and West Indies and their relation to tectonic phenomena.* Doctor VENING MEINESZ has developed a new and accurate method for measuring gravity at sea. During the past decade he has travelled 50,000 miles in submarines and has occupied many hundreds of gravity stations at sea. His work is of great importance to geodesy and to our knowledge of isostasy, tectonics, and the shape of the earth.

After a brief intermission the address was followed by the 34th annual meeting of the Academy, which was called to order by Vice-President H. L. CURTIS.

The report of the last annual meeting was read by the Recording Secretary and approved. The report of the Corresponding Secretary, PAUL E. HOWE, showed the membership of the Academy on January 1, 1932, to consist of 15 honorary members, 3 patrons, and 569 members, one of whom was a life member; a total of 587, of whom 384 reside in or near the District of Columbia, 28 in foreign countries, and 175 in other parts of the continental United States. The members of the Academy stood in respect to the memory of those who had died during the year: EDWARD GOODRICH ACHESON, New York City, July 6, 1931; HENRY MARC AMI, Ottawa, Canada, January 4, 1931; J. W. GIDLEY, Washington, September 26, 1931; ALFRED JUDSON HENRY, Washington, October 5, 1931; HOWARD L. HODGKINS, Washington, February 13, 1931; GEORGE MARTIN KOBER, Washington, May 24, 1913; RUSSELL A. OAKLEY, Washington, August 6, 1931; L. H. PAMMEL, Ames, Iowa; HENRY MARTIN PAUL, Washington, March 15, 1931; R. A. F. PENROSE, JR., Philadelphia, Pa., July 30, 1931. Honorary Members: F. WIGGLESWORTH CLARKE, Washington, May 23, 1931; RAOUL GAUTIER, Switzerland, April 9, 1931, DAVID STARR JORDAN, Stanford University, September 19, 1931.

The report of the Recording Secretary showed 8 scientific meetings during the year of which three were joint meetings. The meetings and abstracts of the addresses given at these meetings, have been filed and published in the Journal of the Academy. The report was approved.

The report of the Treasurer, H. G. AVERS, showed $6,712.14 to be accounted for with disbursements of $4,843.45 and a bank balance of $1,868.69 on December 31, 1931. Assets were listed as $23,074.12.

The report of the Auditors consisting of approval of the report of the Treasurer, was read and both reports were accepted and filed.

The Senior Editor of the Journal, C. WYTHE COOKE, submitted the following record of the twenty-first year of publication of the Journal:

Volume 21 consists of 552 pages, containing 41 papers by members and

39 communicated papers, and being illustrated by 14 half-tones and 47 line engravings. Relative to the number of pages occupied by them these papers were distributed as follows: 5 mathematical or physical papers, 32.8; 5 papers on chemistry, physical chemistry, or crystallography, 35.6; 14 papers on geophysics, geology, paleontology, or paleobotany, 101.1; 18 papers on botany, 108.5; 35 zoological papers, totaling, 140.6; 3 papers on archeology, ethnology, or necrology, 11.0.

This report was approved.

Mr. O. H. GISH, Chairman of the Teller's Committee, reported 270 ballots counted. The following officers were elected: L. H. ADAMS, *President;* W. F. EICHELBERGER and W. H. WILMER, *Non-resident Vice-Presidents;* PAUL E. HOWE, *Corresponding Secretary;* CHARLES THOM, *Recording Secretary;* H. G. AVERS, *Treasurer;* C. WYTHE COOKE and J. A. FLEMING, *Managers* for the term of three years ending January, 1935.

The Corresponding Secretary reported the following members as nominated for *Vice-Presidents* by the affiliated societies. Upon motion the Secretary was directed to cast one ballot for the election of the list as read: *Anthropological*, Mr. N. M. JUDD;[1] *Archaeological*, Dr. WALTER HOUGH; *Bacteriological*, Dr. L. A. ROGERS; *Biological*, Mr. H. H. T. JACKSON; *Botanical*, Dr. H. B. HUMPHREY; *Chemical*, Dr. EDWARD WICHERS; *Electrical Engineers*, Dr. EUGENE C. CRITTENDEN; *Engineers*, Prof. O. B. FRENCH; *Entomological*, Dr. HAROLD MORRISON; *Foresters*, Dr. F. C. CRAIGHEAD; *Geographic*, Dr. F. V. COVILLE; *Geological*, Mr. O. E. MEINZER; *Helminthological*, Dr. G. STEINER; *Historical*, Mr. ALLEN CLARK; *Mechanical Engineers*, Dr. H. L. WHITTEMORE; *Medical*, Dr. HENRY C. MACATEE; *Military Engineers*, Col. C. H. BIRDSEYE; *Philosophical*, Dr. H. L. CURTIS.

Past President HUMPHREYS was delegated to escort President L. H. ADAMS to the chair. President ADAMS addressed the Academy briefly and declared the meeting adjourned at 9:55 P.M.

CHARLES THOM, *Recording Secretary.*

RECENTLY ELECTED TO MEMBERSHIP IN THE WASHINGTON ACADEMY OF SCIENCES

HONORARY MEMBER

Sir JAMES HOPWOOD JEANS has been made an Honorary Member in recognition of his contributions to the dynamical theory of gases, to cosmogony, and to astrophysics. His brilliant applications of mathematical physics to the problems of astronomy have made him one of the leaders in the recent great advance in that science. Among his important publications are the following books: *The Dynamical Theory of Gases, Problems in Cosmogony and Stellar Dynamics*, and *Astronomy and Cosmogony*. He is a Research Associate of the Carnegie Institution of Washington.

MEMBERS

Dr. FREDERICK SUMNER BRACKETT, director of the Division of Radiation and Organisms, of the Smithsonian Institution. Dr. BRACKETT is well known for his investigations in spectroscopy, including the development of thermopiles, and for his researches on plants and radiation, the results of which have been published in various journals.

[1] Elected by Board of Managers.

Dr. ROBERT HERMAN BOGUE, research director, Portland Cement Association Fellowship at the Bureau of Standards. Dr. BOGUE was elected to membership in recognition of his contributions to colloid chemistry and to the physical chemistry of silicates. He is the author of numerous papers on these subjects.

Prof. OAKES AMES, Professor of Botany, Supervisor of Biological Laboratory and Botanical Garden (Cuba), Arnold Arboretum and Botanical Museum, Harvard. Prof. AMES was elected to membership in recognition of his contributions to systematic orchidology. He is the preeminent authority in this large and exceedingly difficult group of plants.

Dr. THOMAS BARBOUR, director, Museum of Comparative Zoology. Dr. BARBOUR was elected to membership in recognition of his contributions to herpetology and ornithology.

Dr. JOHANNES HADELN BRUUN, Research Associate at the Bureau of Standards. Dr. BRUUN was elected to membership in recognition of his work on the separation and identification of the constituents of petroleum, the results of which have been published in various journals.

CHARLES ALLEN CARY, Physiological Chemist, Research Laboratories, Bureau of Dairy Industry. Mr. CARY was elected to membership in recognition of his contributions to the knowledge of nutrition and particularly the protein metabolism of milking cows. He is the author of numerous papers on these subjects.

HENRY B. COLLINS, JR., Assistant Curator, Division of Ethnology, U. S. National Museum. His election to membership was in recognition of his archeological researches in the southeastern section of the United States and in Alaska, and his contributions to physical anthropology.

Dr. JAMES FITTON COUCH, Chemist, Bureau of Animal Industry. Dr. COUCH was elected to membership in recognition of his work on the active principles of stock-poisoning plants. The results of his work have been published in various journals and bulletins.

Dr. CARL S. CRAGOE, Physicist, Bureau of Standards. Dr. CRAGOE was elected to membership in recognition of his work on the thermodynamic properties of ammonia and of petroleum products.

Dr. LEON FRANCIS CURTISS, Physicist, Bureau of Standards. Dr. CURTISS was elected to membership in recognition of his investigations in radioactivity and cosmic radiation.

Dr. FRANCIS MARION DEFANDORF, Physicist, Bureau of Standards. Dr. DEFANDORF was elected to membership in recognition of his contributions to the science of electrical measurements, particularly in the field of high voltage.

HERBERT N. EATON, Acting Chief of the hydraulic laboratory, Bureau of Standards. Mr. EATON was elected to membership in recognition of his work in aeronautics and hydraulics. He has written numerous articles on aeronautic instruments.